PATENT COOPERATION TREATY

09/674994
50CO

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 13 November 2000 (13.11.00)	
International application No. PCT/IB99/01266	**Applicant's or agent's file reference** 109289105PCT
International filing date (day/month/year) 13 May 1999 (13.05.99)	**Priority date** (day/month/year) 13 May 1998 (13.05.98)
Applicant ALPEROVICH, Mark et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

10 December 1999 (10.12.99)

[ ] in a notice effecting later election filed with the International Bureau on:

____

2. The election [X] was
[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING AMENDMENTS OF THE CLAIMS

(PCT Rule 62 and Administrative Instructions, Section 417)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as International Preliminary Examining Authority

Date of mailing (day/month/year) 13 November 2000 (13.11.00)	
International application No. PCT/IB99/01266	International filing date (day/month/year) 13 May 1999 (13.05.99)
Applicant OMD DEVICES LLC et al	

The International Bureau hereby informs the International Preliminary Examining Authority that no amendments under Article 19 have been received by the International Bureau (Administrative Instructions, Section 417).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer Olivia TEFY Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

COHEN, Herbert
Blank Rome Comisky & McCauley LLP
Suite 1000
900 17th Street, N.W.
Washington, DC 20006
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 21 November 2000 (21.11.00)	
Applicant's or agent's file reference 109289105PCT	**IMPORTANT NOTIFICATION**
International application No. PCT/IB99/01266	**International filing date** (day/month/year) 13 May 1999 (13.05.99)

1. The following indications appeared on record concerning:

[X] the applicant [X] the inventor [ ] the agent [ ] the common representative

Name and Address	
LEVICH, Eugene Apartment 9L 330 West 45 Street New York, NY 10036 United States of America	State of Nationality / State of Residence Telephone No. Facsimile No. Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

Name and Address	
LEVICH, Eugene Apartment 9L 235 West 76th Street New York, NY 10023 United States of America	State of Nationality / State of Residence Telephone No. Facsimile No. Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Anman QIU Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

COHEN, Herbert
Blank Rome Comisky & McCauley LLP
Suite 1000
900 17th Street, N.W.
Washington, DC 20006
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (day/month/year) 23 December 1999 (23.12.99)	
Applicant's or agent's file reference 109289105PCT	**IMPORTANT NOTIFICATION**
International application No. PCT/IB99/01266	**International filing date** (day/month/year) 13 May 1999 (13.05.99)

1. The following indications appeared on record concerning:
[X] the applicant [X] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
ZUHL, Irene Yoav Ben Tzruya Street 10/3 77535 Ashdid Israel	IL	IL
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:
[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

Name and Address	State of Nationality	State of Residence
ZUHL, Irene Yoav Ben Tzruya Street 10/3 77535 Ashdod Israel	IL	IL
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[ ] the International Preliminary Examining Authority
[X] the designated Offices concerned
[ ] the elected Offices concerned
[ ] other:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Aino Metcalfe Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

COHEN, Herbert
Blank Rome Comisky & McCauley LLP
Suite 1000
900 17th Street, N.W.
Washington, DC 20006
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 21 November 2000 (21.11.00)	
Applicant's or agent's file reference 109289105PCT	**IMPORTANT NOTIFICATION**
International application No. PCT/IB99/01266	**International filing date** (day/month/year) 13 May 1999 (13.05.99)

1. The following indications appeared on record concerning:

[X] the applicant [X] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
LEVICH, Eugene Apartment 9L 330 West 45 Street New York, NY 10036 United States of America		
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

Name and Address	State of Nationality	State of Residence
LEVICH, Eugene Apartment 9L 235 West 76th Street New York, NY 10023 United States of America		
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Anman QIU Telephone No.: (41-22) 338.83.38

10 RN
09/674994
5040

14

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

RECD 27 MAR 2001
WIPO PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 109289105PCT	**FOR FURTHER ACTION** See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IB99/01266	International filing date *(day/month/year)* 13 MAY 1999	Priority date *(day/month/year)* 13 MAY 1998
International Patent Classification (IPC) or national classification and IPC IPC(7): B32B 3/00 and US Cl.: 428/64.1		
Applicant OMD DEVICES LLC		

RECEIVED

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets.

   ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report
   II ☐ Priority
   III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   VI ☐ Certain documents cited
   VII ☐ Certain defects in the international application
   VIII ☐ Certain observations on the international application

Date of submission of the demand 10 DECEMBER 1999	Date of completion of this report 09 MARCH 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ELIZABETH EVANS Jean Proctor Paralegal Specialist Telephone No. (703) 308-0661

Form PCT/IPEA/409 (cover sheet) (July 1998)★

THIS PAGE BLANK (USPTO)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/IB99/01266

I. Basis of the report

1. With regard to the **elements** of the international application:*

[X] the international application as originally filed

[X] the description:
pages 1-15, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of

[X] the claims:
pages 16-18, as originally filed
pages NONE, as amended (together with any statement) under Article 19
pages NONE, filed with the demand
pages NONE, filed with the letter of

[X] the drawings:
pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of

[X] the sequence listing part of the description:
pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language ________ which is:

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application (under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

[ ] contained in the international application in printed form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. [X] The amendments have resulted in the cancellation of:

[X] the description, pages NONE

[X] the claims, Nos. NONE

[X] the drawings, sheets/~~fig~~ NONE

5. [ ] This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

***Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/IB99/01266

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	NONE	YES
	Claims	1-10	NO
Inventive Step (IS)	Claims	NONE	YES
	Claims	1-10	NO
Industrial Applicability (IA)	Claims	1-10	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-10 lack novelty under PCT Article 33(2) as being anticipated by SANTO.

SANTO discloses an optical recording medium comprising a dye-in-polymer recording layer where the dye is a fluorescent dye such as xanthene, cyanine or phthalocyanine and the polymer binder may be a resin such as cellulose ether, ethyl cellulose, polyvinyl alcohol, etc. See column 4, lines 18-35 and column 6, lines 25-68. The recording layer also contains a compound capable of generating free radicals such as triphenylmethylbenzene. See column 4, lines 45-68. The recording layer may be formed of two sublayers and may contain non-fluorescent dyes.

Claims 1-10 meet the criteria set out in PCT Article 33(3)-(4) because they have utility in the recording art.

-------------------- NEW CITATIONS --------------------
NONE

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/IB99/01266

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

Form PCT/IPEA/409 (Supplemental Box) (July 1998)

CORRECTED VERSION*

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : **B32B 3/00**	A3	(11) International Publication Number: **WO 99/59142** (43) International Publication Date: 18 November 1999 (18.11.99)

(21) International Application Number: PCT/IB99/01266

(22) International Filing Date: 13 May 1999 (13.05.99)

(30) Priority Data:
60/085,334 13 May 1998 (13.05.98) US

(71) Applicant (*for all designated States except US*): OMD DEVICES LLC [US/US]; 1013 Centre Road, Wilmington, DE 19805 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): ALPEROVICH, Mark [IL/IL]; Hamelech Hizkija 33/3, 77497 Ashdod (IL). LEVICH, Eugene [IL/US]; Apartment 9L, 330 West 45 Street, New York, NY 10036 (US). ZUHL, Irene [IL/IL]; Yoav Ben Tzruya Street 10/3, 77535 Ashdod (IL). MAKIEVSKAYA, Svetlana [IL/IL]; Mamapilim Street 20, 77497 Ashdod (IL).

(74) Agents: COHEN, Herbert et al.; Blank Rome Comisky & McCauley LLP, Suite 1000, 900 17th Street, N.W., Washington, DC 20006 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(88) Date of publication of the international search report: 29 June 2000 (29.06.00)

(54) Title: ORGANIC DYE-IN-POLYMER (DIP) MEDIUM FOR WRITE-ONCE-READ-MANY (WORM) OPTICAL DISCS WITH FLUORESCENT READING

(57) Abstract

High sensitive organic dye-in-polymer (DIP) medium for write-once-read-many (WORM) optical discs with fluorescent reading. The medium consists of a fluorescent color means, capable of absorbing writing radiation produced by a laser, a compound capable of generating free radicals upon influence of heat produced by the writing radiation and a polymer capable of producing a translucent film enabling high quantum yield of the fluorescence induced in the color means. The color means can be selected from xanthene dyes of the eosine and rhodamine groups, acridine, oxazine, azine, peylene, violanthrone, cyanine, phtalocyanine, indigoide colors and porphyries. The free radicals generating compound can be chosen from the group of compounds comprising azo and diazoi compounds or peroxyde compounds. The film producing polymer can be selected from the group of compounds comprising cellulose ethers, vinyl resins or acrylic resins.

*(Referred to in PCT Gazette No. 30/2000, Section II)

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

ORGANIC DYE-IN-POLYMER (DIP) MEDIUM FOR WRITE-ONCE-READ-MANY (WORM) OPTICAL DISCS WITH FLUORESCENT READING

Field of the invention

This invention is in the field of media for WORM optical discs with fluorescent reading, providing high capacity optical memory, including 3-dimensional optical memory systems.

Background of the Invention

Recently WORM optical memory devices have experienced great evolution, providing recording of data with the possibility of its immediate reading. This feature – data recording in a real-time regime – is significant for various applications of optical recording in memory devices, especially for computer systems. For this field duplication of data is not so essential.

All WORM optical media of practical interest is based on photothermal principle of recording. The data on such media is recorded by scanning the recording layer with the focused laser beam. The laser power is absorbed by the active medium of the layer and transformed into thermal energy, causing its physical and chemical changes, which can be optically registered at reading.

Photochemical effects can also be used, i.e. optically detected changes in the state of medium, caused by direct interaction of photons with this medium. The efforts are made to use photosensitive medium for photochemical recording on WORM discs. Hence, until now there was no practical application for WORM discs with photon mechanism of recording. The reason can be the non-threshold nature of photochemical recording on the contrary to photothermal recording at the same laser for recording and

reading (with different laser power). Therefore, the photochemical recording can not provide the necessary stability of medium characteristics at multiple reading.

According to the mechanisms of thermally induced effects, the photothermal recording on WORM optical medium with practical applications can be divided in two parts:

1. Ablative, providing optically registered geometric changes in the thin active layer during its melting, evaporation or chemical transformations, and
2. With phase change, which does not provide geometric changing of the active layer, otherwise changing its optical constants, that causes optical contrast, which is usually not high for these materials.

Among various types of medium for ablative recording, WORM optical discs with thin (10-100 nm) layers of organic dyes with or without dye-in-polymer are of special interest. Layers of organic dyes provide a range of sufficient advantages in comparison to metal or half-metal layers, used in WORM discs with ablative recording. Advantages are the following:

- Dyes may have a stronger selective absorption on the recording laser wavelength.
- Dye layers are more sensitive to the laser radiation because of their small thermal conductivity and low temperature of melting or decomposition. It provides a higher recording capacity.
- Dye layers provide a higher stability at higher humidity.
- Medium based on dye layers has better signal-to-noise ratio, because of the lack of noise, provided by amorphous layers.
- Coating in the centrifuge makes the layers, that is more simple and cheap than vacuum deposition used for obtaining metal and half-metal layers on WORM discs.

The existing WORM optical discs based on organic dyes has a capacity up to 3.5 GB.

The WORM discs with one recording layer this optical memory capacity is the utmost at least for the diode laser with 780-830 nm wavelength.

Future capacity increase for WORM discs is possible only using three-dimensional optical memory carriers with multilayer data recording and fluorescent reading [A.S. Dvornikov, P.M. Rentzepis, Opt. Comms., v.136, pp. 1-6 (1997); B. Glushko, US Provisional Patent Application, May 8, 1997, N 25457.].

Fluorescent reading offers a range of sufficient advantages in comparison to reading, based on changing the reflection ratio, even in single-layer systems.

One of the advantages is the reduced tolerance for the sizes of recorded pits in comparison to the existing WORM discs. I.e., changing the size on a 100 nm does not influence the reading from fluorescent disc, while it totally eliminates the signal from reflective discs.

Another advantage is the reduced sensitivity of fluorescent discs to changing the slope up to 1 grad that is absolutely intolerable for reflective discs.

Nevertheless, the basic advantage of fluorescent reading is the enhanced capacity of three-dimensional optical memory carriers, realized as multilayer discs.

Use of layers of organic dyes with ablative recording in such medium is not possible owing to the following reasons:

- Reading is realized by laser beam, scanning the change of reflection in the pre-irradiated spots. In a multilayer system, this method causes a strong fall of reading quality, becoming dramatic for systems with over four active layers.
- Heat change of the layer geometrical structure at recording, such as: burning out of holes, creation of bubbles, change of surface texture, etc. It is also unsuitable for

multilayer medium, as it causes dispersion of the reading beam, hence abruptly lowering the level of fluorescent signal.

- The dye concentration in the recording layer of the existing WORM discs is the utmost (up to 99%). In this case, the dye fluorescence is usually suppressed because of high concentration.

In the thin dye layers (10-100 nm) of the existing WORM discs the local heating of the medium at recording can reach 700°C. Such high temperature make it difficult to avoid changing the geometrical structure of the layer. Increase of the dye layer thickness up to 200 nm and more using polymer dye at preserving the surface concentration of dye leads to lowering the local heating temperature and allows to prevent the layer deformation. It also provides the appearance and growth of the dye fluorescence due to lowering the concentration suppression effect. However at all the same conditions the layer sensitivity to laser radiation is dramatically lowering, that leads to drop of recording speed and density.

Thus, all the known materials, used for single-layer optical WORM discs with reflective reading, as well as photothermal recording methods can not be used for multilayer optical WORM discs with fluorescent reading. Comparatively thick layers (200 nm and more) of fluorescent dye are likely not suitable for multilayer medium as well without use of special additives and ways of recording, increasing recording speed and density.

Summary of the Invention

Considering the above-stated, the purpose of this Invention is the obtaining of a high-sensitive organic dye-in-polymer (DIP) medium for write-once-read-many (WORM) optical discs with fluorescent reading, providing high speed and density of photothermal recording.

The other purpose of the present Invention is the obtaining of a DIP environment with high sensitivity to the recording laser radiation in visual and infra-red range.

The future purpose of the present Invention is the obtaining of a DIP environment for single- and multilayer mediums with high optical memory capacity and high signal-to-noise ratio.

According to the purpose of the present Invention, the above-stated DIP environment contains a fluorescent dye, capable to absorb the recording laser radiation and to transform the absorbed light power into heat, and a choice of substances, capable to generate free radicals at their decomposition under heating, received from the laser radiation absorption by the fluorescent dye.

According to the other purpose of the present Invention, the above-stated DIP environment contains a fluorescent dye and a non-fluorescent dye, capable to absorb the recording laser radiation and to transform the absorbed light power into heat, and a choice of substances, capable to generate free radicals at their decomposition under heating, received from the laser radiation absorption by the non-fluorescent dye.

According to the future purpose of the present Invention, the above-mentioned free radicals cause the discoloring or change of absorption spectrum range of the fluorescent and/or non-fluorescent dyes, thus making the recording.

If the discoloring or change of color of the fluorescent and/or non-fluorescent dyes makes the recording, absorption and fluorescence spectrum ranges of the first dye can just slightly overlap the absorption spectrum of the second dye. In this case, the layer is fluorescent before recording. After recording is made, the irradiated spots lose fluorescence, while the background remains fluorescent.

If the discoloring or change of color of only the non-fluorescent dye makes the recording, than its absorption spectrum range shall overlap the absorption and/or fluorescence spectrum of the fluorescent dye. In this case, the layer is not fluorescent before recording. After recording is made, the irradiated spots become fluorescent, while the background is not fluorescent.

Detailed Description of the Preferred Embodiments

Below there is a detailed description of the mostly preferred ways to reach the intended purposes of the Invention.

First we shall consider the variant when the substrate - a transparent disc from glass, polymethylmethacrylate, polycarbonate or polyethylene terephthalate - is covered with a recording layer, consisting of at least a fluorescent dye, capable to absorb the recording laser radiation, a compound, capable to generate free radicals during decomposition under heating, received from the laser radiation absorption by the fluorescent dye, and a film-forming polymer with high transparency, low heat conductivity and capable to provide the necessary quantum output of the dye fluorescence.

Besides, the recording layer can contain compounds, quickening or suppressing photothermal decoloration of the dye, plastifiers, surface-active substances, organic reducers, preventing free radicals oxygen deactivation, etc.

The thickness of recording layer can be 100-1000 nm, preferably - 200-500 nm. Fluorescent dye with absorption maximum near the recording laser wavelength is chosen among the xanthene dyes of the eosin and rhodamine groups, acridine, Oxazine, azine, perylene, violanthrone, cyanine, phthelocyanine dyes, indigoide colors and porphyries.

The content of fluorescent dye in the layer is equal to 0,1-10%.

The choice of compound, capable to generate free radicals during decomposition under heating, received from the laser radiation absorption by the fluorescent dye, shall consider the relevant temperatures and rate of its decomposition. The possible compounds, capable to generate free radicals, are azo and diazo compounds such as azo-bisisobutyronitrile, p-bromobenzene diazohydroxide, triphenylmethylazibenzene and diazobenzoyl, nitrosoacetanilide and its derivatives; peroxides such as benzyl peroxide and its derivatives, tert-dibutyl peroxide, etc.

The content of compound, capable to generate free radicals, in the recording layer is equal to 0,1-20%.

The free radicals, appearing during thermal decomposition of the above-mentioned compounds, are extremely reactive towards organic substances. One of the typical reactions with free radicals is their chain bonding to olefin bond.

This reaction is one of the main reasons for decoloration of organic dyes. The free radicals interact with olefin linkages of the dye, making the dye molecules decay, what leads to decoloration or change of color.

The film-forming polymer can be selected from a wide range of resins, such as: cellulose esters, i.e. nitrocellulose, cellulose acetate, cellulose acetate butyrate; cellulose ethers, i.e. methyl cellulose, ethyl cellulose, butyl cellulose; vinyl resins, i.e. polyvinyl acetate, polyvinyl butyral, polyvinyl acetyl, polyvinyl alcohol and polyvinyl pyrrolidon; acrylic resins, i.e. polymethylmetacrylate, polybutyl acrylate, polymethacylic acid, polyacryl amid polyacrylonitrile.

Film-forming properties of the used resins and the plasticity of the recording layer can be improved by adding to resins the proper plastifier, such as dibutyl phthalate, dioctyl phthalate or tricresyl phosphate.

Zinc, lead, or cadmium salts of the higher aliphatic acids and also urea and etanolamine can be used for lowering decomposition temperature of compounds, generating free radicals, and therefore quickening the decoloring process.

Hydroquinone, aliphatic and heterocyclic amines, sulfur containing compounds such as thiols, sulfides, disulfides isothiocyanates can be used to slow down decomposition of the compounds, generating free radicals.

Reducing amines can also be added to prevent free radicals oxygen deactivation. They can be n-butylamine, dimethylaminoethyl methacrylate, diethyl-n-butylphosphine, and isoamyl 4-dimethylaminobensoate.

To create a recording layer of the present Invention, the above-mentioned ingredients are dissolved in organic solvent or introduced in it as microcapsules less than 0,2 mkm in size, prepared by known methods, with future covering the substrate with this compound by spin coating, roller coating or dip coating.

The organic solvent is usually selected from alcohols, ketones, amides, sulfoxides, ethers, esters, halogenated aliphatic hydrocarbons or aromatic solvents. Examples of such solvents include methanol, ethanol, iso-propanol, iso-butanol, tetrafluoro-ethanol, diacetone alcohol, methyl cellosolve, ethyl cellosolve, acetone, methylethylketone, cyclohexanone, N,N-dimethhyl-formamide, N,N-dimethylacetamide, dimethylsulfoxide, tetra-hydrofurane, dioxane, ethyl acetate, chloroform, methylene chloride, dichloroethane, toluene, xylene or their mixtures.

In the other variant of realizing purposes of this Invention the recording layer also contains a non-fluorescent dye with an absorption spectrum range just slightly overlapping the absorption and fluorescence spectrum range of the fluorescent dye and with the maximum absorption value being close to the recording laser wavelength. The layer is fluorescent in its initial state before recording. During recording the non-

fluorescent dye absorbs the laser radiation and transforms the absorbed light power into heat, influencing the generation of free radicals, causing decoloration of the fluorescent dye.

(The non-fluorescent dye can also lose color, what does not effect the use features of the medium.) After recording the irradiated spots has no fluorescence, while the background remains fluorescent. The advantage of this variant in comparison to the previous one is that the non-fluorescent dye is more effective in transforming light power to heat, than the fluorescent one, hence in this case we are to use lasers with different wavelength for recording and reading.

In the other variant of realizing purposes of this Invention the recording layer also contains a non-fluorescent dye with an absorption spectrum range covering the absorption and/or fluorescence spectrum range of the fluorescent dye. Concentration of the fluorescent dye shall provide a non-fluorescent layer before recording. Absence of fluorescence in the case, when absorption spectrum range of the non-fluorescent dye overlaps the absorption spectrum range of the fluorescent dye is caused by the fact that absorption optical density of the 1st dye is much higher than the 2nd one.

If the non-fluorescent dye absorption spectrum overlaps with the fluorescent dye absorption spectrum, absence of fluorescence is provided by non-radiating intermolecular electronic excitation energy transfer from the second dye D* to the first A upon the Firster's resonance mechanism. This energy transfer process is schematically described by the following equations:

D + hv ------- D*

D* + A -------- A* + D,

where the * means the electronically excited state.

At recording, the fluorescent and non-fluorescent dyes absorb laser radiation and transform the absorbed light power into heat, which influences the generation of free

radicals, causing decoloration of the non-fluorescent dye. After recording, the irradiated spots become fluorescent. It allows to use the same laser (but with different pulse power) for recording and reading.

In the present Invention the single recording layer of the optical disc is either directly deposited on the substrate, or there is also an intermediate layer between the substrate and the recording layer, that improves adhesion and mechanical solidity and lowers heat losses, preventing heat distribution into the substrate. Besides, use of intermediate layer can allow adding into the recording layer the solvents, being aggressive to the substrate.

Besides, the recording layer can consist of two polymer sub-layers, one containing dyes, and the other containing the compound, generating free radicals, with the latter positioned above or below the sub-layer with dyes.

The recording layer can be covered with a protective layer or another substrate can be bonded on it to protect the recording layer against the external environment and to improve its safety.

For obtaining a multilayer disc for three-dimensional optical memory with fluorescent reading the present Invention proposes consecutive bonding of the described above single-layer discs one to another so that the active recording layers would alternate the inactive separating layers of substrate.

For obtaining a multilayer disc the glues shall be used, providing good adhesion of the bonded surfaces and absence of contraction, not influencing negatively the properties of recording layers, not lowering signal-to-noise ratio, transparent for the laser wavelength and fluorescent light. Examples of such glues include UV-hardened optical glues of 3-92, UV-71, UV-69, UV-74, J-91, VTC-2, SK-9 types («Catalog of Summers laboratories»).

Consecutive scanning of every recording layer by a focused laser beam makes the data recording on a multilayer disc. The same way the reading is made.

Example 1.

To obtain the recording layer medium we prepared the methylene chloride solution, containing as film-forming resin – 1% polymethylmethacrylate (PMMA), as fluorescent dye – 0,013% Oxazine 625 Perchlorate with λmax. abc. = 645 nm and λmax. fluor. = 680 nm (Exciton, Inc.) and as a compound generating free radicals – 0,03% benzyl peroxide. The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 2.

To obtain the recording layer medium we prepared the methylene chloride solution, containing as film-forming resin – 1% polymethylmethacrylate (PMMA), as fluorescent dye – 0,01% HIDC Iodide with λmax. abc. = 641 nm and λmax. fluor. = 680 nm (Exciton, Inc.) and as a compound generating free radicals – 0,03% benzyl peroxide. The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 3.

To obtain the recording layer medium we prepared the methylene chloride solution, containing 1% polymethylmethacrylate (PMMA), as fluorescent dye – 0,009% HITC Iodide with λmax. abc. = 751 nm and λmax. fluor. = 790 nm (Exciton, Inc.) and as a compound generating free radicals – 0,002% benzyl peroxide. The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 4.

To obtain the recording layer medium the polyvynilacetate (1%), Oxazine 725 Perchlorate (0,013%), plasticizer – dioctyl phthalate (0,2%) and benzyl peroxide (0,03%) were dissolved in a mixture of ethanol, ethyl cellosolve, iso-propanol, and iso-butanol (4:2:1:1). The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 5.

To obtain the recording layer medium the polyvynilacetate (1%), HIDC Iodide (Exciton, Inc.) (0,01%), dioctyl phthalate (0,2%) and benzyl peroxide (0,003%) were dissolved in a mixture of ethanol, ethyl cellosolve, iso-propanol, and iso-butanol (4:2:1:1). The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 6.

To obtain the recording layer medium the polyvynilacetate (1%), HITC Iodide (Exciton, Inc.) (0,009%), dioctyl phthalate (0,2%) and benzyl peroxide (0,002%) were dissolved in a mixture of ethanol, ethyl cellosolve, iso-propanol, and iso-butanol (4:2:1:1). The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 7.

The same as in examples 1-6, only benzyl peroxide was not dissolved in the compound for the recording layer, but was introduce in it as microcapsules with average diameter 0,1 mkm.

Example 8.

The same as in examples 1,2,4,5, only the recording layer had two sub-layers. The lower sub-layer of 250 nm thickness contained fluorescent dye, while the upper sub-layer of 250 nm thickness contained benzyl peroxide – as the substance generating free radicals at high temperature. All the other mentioned additives were equally distributed in the two sub-layers.

Example 9.

The same as in examples 1,2,4,5, only the recording layer had two sub-layers. The lower sub-layer of 250 nm thickness contained benzyl peroxide – as the substance generating free radicals at high temperature, while the upper sub-layer of 250 nm thickness contained fluorescent dye. All the other mentioned additives were equally distributed in the two sub-layers.

Example 10.

The same as in examples 8 and 9, only the sub-layer containing the substance generating free radicals at high temperature, also contained a non-fluorescent dye – Tetra-phenyl nickel dithiolene (λ max. abs. = 860 nm). In this case, a diode laser with the 830 nm wavelength made the recording, the reading being made at 650 nm laser wavelength.

Example 11.

The same as in examples 1,2,4,5,7-9, only the recording layers and the sub-layers, containing fluorescent dyes with the maximum absorption near the laser wavelength 650 nm, also contains the dye – 1,1',3,3,3',3'-hexamethyl-4,5,4'5'-dibenzo-indodicarbocyanine iodide with λ max. Abc. = 685 nm. In this case recording and reading were made with one laser with 650 nm wavelength.

Example 12.

The same as in examples 1-11, only the recording layers and the sub-layers contained azo-bisisobutyronitrile instead of benzyl peroxide.

Example 13.

For obtaining a multilayer WORM disc 10 single-layer discs, obtained according to one of the examples 1-12, were bonded one after another so that the active recording layers would alternate the inactive separating layers of substrate, using UV-69 glue. The glue was UV-hardened.

Every optical disc obtained according to examples 1-13 was placed on the rotating table, rotated with the speed of 1800 rpm, and recorded by focused pulses of 1 MHz frequency, received from a semiconductor laser with 830 or 650 nm wavelength. The recording power was 30-60 mJ/cm^2. For comparison, we took a standard CD-R disc by TDK with ablative recording and reflective reading. An optical microscope was use to follow physical and chemical changes of the layer after recording.

This discovered decoloration of the dye on the studied examples on the irradiated spots. As a result, on the examples 1-10 and relevant examples 12 and 13 the recorded spots were not fluorescent, while the background remained fluorescent. On the example 11 and relevant examples 12 and 13, the recorded spots were fluorescent, while the background was not. The observation showed no change in the geometrical structure of the recording layer. Under the same conditions, the standard CD-R disc was ablatively recorded by thermoperforation. The signal-to-noise ratio on the studied examples was higher than on the CD-R disc and equal to 4-6.

Thus, the trials under study of the obtained examples have shown their enough sensitivity to the recording laser radiation of visible and infra-red range, high speed and

density of photothermal recording and their suitability for data recording and fluorescent reading on the existing drivers with some small construction changes.

What is claimed is:

1. Dye-in-polymer (DIP) medium for the recording layer of write-once-read-many (WORM) optical disks with fluorescent reading, containing:

- fluorescent dye, capable to absorb the recording laser radiation;
- compound, capable to generate free radicals as a result of decomposition under heating, induced by laser radiation absorption by fluorescent dye;
- film-forming polymer with high transparency, low heat conductivity and providing the necessary quantum output of the dye fluorescence.

2. DIP medium for the recording layer according to item 1, with the difference that its fluorescent dye is chosen from xanthene dyes of the eosin and rhodamine groups, acridine, Oxazine, azine, perylene, violanthrone, cyanine, phthalocyanine dyes, indigoide colors and porphyries. The content of fluorescent dye in the layer is equal to 0,1-10%.

3. DIP medium for the recording layer according to item 1, with the difference that its compound generating free radicals is chosen from azo-bisisobutyronitrile, p-bromobenzene diazohydroxide, triphenylmethylazibenzene and diazobenzoyl, nitrosoacetanilide and its derivatives; peroxides such as benzyl peroxide and its derivatives, tert-dibutyl peroxide, etc. The content of compound, capable to generate free radicals, in the recording layer is equal to 0,1-20%.

4. DIP medium for the recording layer according to item 1, with the difference that the film-making polymer is chosen from resins, such as cellulose esters, i.e. nitrocellulose, cellulose acetate, cellulose acetate butyrate; cellulose ethers, i.e. methyl cellulose, ethyl cellulose, butyl cellulose; vinyl resins, i.e. polyvinyl acetate, polyvinyl butyral, polyvinyl acetyl, polyvinyl alcohol and polyvinyl pyrrolidon; acrylic resins, i.e. polymethylmetacrylate, polybutyl acrylate, polymethacylic acid, polyacryl amid polyacrylonitrile.

5. DIP medium for the recording layer according to item 1, with the difference that the recording layer also contains a non-fluorescent dye with an absorption spectrum range just slightly overlapping with the absorption and fluorescence spectrum ranges of the fluorescent dye and with the maximum absorption value being close to the recording laser wavelength.

6. DIP medium for the recording layer according to item 1, with the difference that the recording layer also contains a non-fluorescent dye with an absorption spectrum range overlapping the absorption and/or fluorescence spectrum range of the fluorescent dye.

7. Method of obtaining a single-layer optical WORM disc, which proposes to dissolve the compounds described in item 1 in an organic solvent, chosen from alcohols, ketones, amides, sulfoxides, ethers, esters, halogenated aliphatic hydrocarbons or aromatic solvents, or to introduce the compounds into solvent as microcapsules less than 0,2 mkm in size, prepared by known methods, with future allocation of this composition by spin coating, roller coating or dip coating on the substrate, representing a glass, polymethylmethacrylate, polycarbonate or polyethylene terephthalate disc.

8. Method of obtaining a single-layer optical WORM disc, which proposes creation of a recording layer from two sub-layers, the lower sub-layer containing fluorescent dye, and the upper sub-layer containing the substance generating free radicals at high temperature.

9. Method of obtaining a single-layer optical WORM disc, which proposes creation of a recording layer from two sub-layers, the upper sub-layer containing fluorescent dye, and the lower sub-layer containing the substance generating free radicals at high temperature.

10. Method of obtaining a multilayer optical WORM disc by consecutive bonding of the single-layer discs one to another forming a multilayer system with two and more recording layers, in which recording layers alternate separating layers of substrate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB99/01266

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B32B 3/00
US CL :428/64.1
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/64.1, 64.1, 64.4, 64.8, 690, 913

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,185,233 A (SANTO) 09 February 1993, see entire document.	1-10
A	US 5,506,357 A (NAMBA) 09 April 1996, see abstract.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 APRIL 2000	26 APR 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
ELIZABETH EVANS
Telephone No. (703) 308-0661